



An electrochemical study of the formation of Benzotriazole surface films on Copper, Zinc and a Copper–Zinc alloy

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Abstract

The electrochemical behaviour of Cu, Cu–37Zn and Zn in benzotriazole (BTA) containing chloride solutions was studied and compared using potentiodynamic, cyclic voltammetry and electrochemical impedance spectroscopy. The presence of BTA in the chloride-containing solutions gave rise to higher breakdown potentials, significantly higher polarisation resistances and inhibited the formation of CuCl_2 and zinc-containing corrosion products. These effects were observed for pure Cu, Cu–Zn and to a somewhat lesser extent pure Zn. The electrochemical impedance data were consistent with the formation of a polymeric BTA-containing layer for all three systems.

1. Introduction

Benzotriazole (BTAH), a heterocyclic compound, has been used widely as an effective aqueous corrosion inhibitor for copper ever since the early reports of Cotton and co-workers [1, 2]. The mode of action of this inhibitor has been attributed to the formation of a polymeric-type film comprising Cu(I)–BTA units, in near-neutral solutions [3–7], with ageing favouring this complex formation [8]. Adsorption of BTA at the surface has been proposed as the more favourable mechanism in acidic solutions, at low applied potentials, or when BTA is present in low concentrations [9–11]. It has been shown that the highest degree of corrosion protection is afforded by the thin polymerised film formed on an oxidised Cu surface [12].

Most of the mechanistic studies on the role of BTA in corrosion inhibition have centred on pure copper. However, it has been reported previously that BTA inhibits the electro-dissolution of Co [13], Cu–10Ni [14], Cu–13Sn [15], inhibits the stress corrosion cracking of Cu–30Zn in fluoride solutions [16] and Cu–28Zn in nitrite solutions [17] and inhibits the corrosion of Al-bronze in saline solutions [18]. Chadwick and Hashemi [19] have detected, using X-ray photoelectron spectroscopy, both copper and zinc in surface films formed on Cu–30Zn in chloride-containing BTAH solutions. Gupta et al. [20, 21], in studying the corrosion behaviour of Cu–30Zn in H_2SO_4 , found that BTAH inhibited corrosion of the copper component, but had little effect on the rate of dezincification. Costa et al. [22] suggested that the film formed on Cu–30Zn in H_2SO_4 -containing BTAH solutions consisted of polymeric Cu(I)BTA units. In a later work Costa et al. [23] showed that a

two-stage film dissolution process occurred for Cu–30Zn in the presence of BTA in HCl solution at potentials above the Tafel region. This was attributed to the formation of a duplex film consisting of a porous CuCl outer layer and a Cu(I)–BTA nonporous inner layer.

Despite these investigations, there remains relatively little information on the mode of action of BTA in the corrosion inhibition of zinc-containing copper alloys. Likewise, there is very little data available on the impedance response of Cu–Zn in BTA-containing solutions. In this communication, the role of BTAH in modifying the electrochemical dissolution of a zinc-rich copper alloy, Cu–37Zn, in chloride-containing solutions is investigated using anodic polarisation measurements, cyclic voltammetry and electrochemical impedance spectroscopy and the results are discussed in light of the published works on the pure copper system. For comparative purposes similar experiments were carried out on pure copper and pure zinc.

2. Experimental

Electrodes were prepared from pure zinc (99.999%), pure copper (99.99%) and a zinc-rich copper alloy, Cu63–Zn37. The electrodes were provided in rod form and were embedded in epoxy resin in a Teflon holder with electrical contact being achieved by means of a copper wire threaded into the base of the metal sample. Prior to each test the exposed surfaces were polished to a smooth surface finish, using 1200 g SiC, and rinsed with distilled water. High-density graphite rods were used as the auxiliary electrodes and a saturated calomel electrode (SCE) was used as the reference electrode, with all

potentials represented relative to this electrode. The electrolytes were prepared using analytical grade reagents and distilled water. 0.1 or 0.5 mol dm⁻³ NaCl solutions, adjusted to pH values between 3.0 and 9.0 using either NaOH or HCl were used as the aggressive solution, while the benzotriazole-containing electrolytes consisted of these solutions with the addition of either 0.005 or 0.01 mol dm⁻³ BTA.

Potentiodynamic electrochemical experiments were carried out using an EG&G Potentiostat, PAR Model 263. The working electrodes were polarised from below the corrosion potential at a scan rate of 0.5 mV s⁻¹ in the anodic direction, following polarisation at some cathodic potential. Impedance measurements were recorded using a Solartron 1250 Frequency response analyser and an EI 1287 electrochemical interface. The spectra were recorded at the corrosion potential following different immersion periods under open-circuit conditions. An excitation voltage of 10 mV was used in all tests. All impedance data were fit to appropriate equivalent circuits using a complex non-linear least squares fitting routine, using both the real and imaginary components of the data.

3. Results

In Figure 1 the anodic polarisation behaviours of pure Cu, pure Zn and Cu-37Zn in 0.1 mol dm⁻³ NaCl in the presence and absence of 0.01 mol dm⁻³ BTA are shown. Plots recorded at pH values of 3.5 and 7.8 are shown in (a) for pure Cu, in (b) for Cu-37Zn and in (c) for pure Zn. A significant ennoblement in the breakdown potential is seen for Cu in the presence of BTA, in agreement with several other publications [1–12]. A clear breakdown potential, at 0.59 V(SCE), is seen in the near neutral solution, but in the acidic solution the anodic current only increases slightly, and only exceeds 100 $\mu\text{A cm}^{-2}$ at approximately 1.0 V(SCE). In addition to these more noble breakdown potentials lower corrosion currents, estimated using Tafel Analyses, and slightly reduced cathodic currents were measured in the presence of BTA. The data shown in Figure 1(b) for the Cu-37Zn system do not exhibit the same degree of BTA-induced passivation. However, the breakdown potential is increased by some 350 mV in the near-neutral solution and in excess of 150 mV in the acidic solution in the presence of BTA. In this case, a clearer breakdown potential is seen in the acidic solution, with the current increasing steadily well in excess of 1 mA cm⁻² at 150 mV. It can be seen from the data presented in Figure 1(c) that the presence of BTA in solution exerts some passivating effect on pure Zn. The polarisation plots are shifted in the anodic direction, with the greatest effect being observed in the acidic solution, in the presence of BTA. The data recorded in the more alkaline pH 9.0 BTA solution were similar to those shown for the near-neutral solution. Also, similar effects were observed with BTA in the more concentrat-

ed 0.5 mol dm⁻³ NaCl solution, however under these conditions, the BTA-induced passivation effects were slightly reduced. In all cases, the BTA-induced passivation effects, as evident from these polarisation measurements, decreased in the order Cu > CuZn > Zn.

In Figure 2 impedance data, recorded under open-circuit conditions following a 460-min immersion period, are shown for pure Cu in the pH 3.5 and 7.8 solutions in the presence and absence of BTA. The simulated data, shown by the solid lines, were generated using the equivalent circuits depicted in Figure 2(c). In the case of the acidic solutions, Figure 2(a), the relatively simple circuit, involving the elements R_s , Q_1 , R_1 , and Q_2 , was used in the fitting routine. This same circuit was used to fit the data obtained in the presence of BTA in the near-neutral solution, but the more complex circuit incorporating an additional parallel Q_3 R_2 combination was required in the fitting of the data measured in the pH 7.8-chloride containing solution. In each of these circuits the R terms represent resistor elements, while the Q terms represent constant phase elements (CPE), where the impedance of a constant-phase element, is defined as $Z_{\text{CPE}} = [Q(j\omega)^n]^{-1}$ where $-1 \leq n \leq 1$ [22]. When the value of n approaches unity the CPE is equivalent to a capacitor, while n values close to 0.5 are indicative of diffusion, and consequently the CPE represents a Warburg diffusion component.

It can be seen, from a comparison of the impedance data presented for the acidic solution, that the presence of BTA in solution has a considerable inhibiting effect on the dissolution of copper. The impedance spectra recorded in the presence of BTA are characterised by a medium-frequency capacitive region and a low frequency diffusion region, with the n value for Q_1 being essentially unity and the n value for Q_2 close to 0.5. In this case, Q_1 represents the double layer capacitance, Q_2 represents a Warburg diffusional process and R_1 is the charge transfer resistance. Similar data were recorded in the presence of BTA in the near-neutral solution, Figure 2(b). The spectra recorded in the acidic solution in the absence of BTA are characteristic of a diffusional process that dominates even into the medium frequency region, with the phase angle not exceeding 45°. Here the n value for both Q_1 and Q_2 are close to 0.5. This is consistent with the formation of a cuprous chloride precipitate layer that dominates the impedance response. The data recorded in the neutral solution are dominated, also, by diffusion processes. The n value, calculated in fitting the data, for Q_2 was exactly 0.5, while the n values calculated for Q_1 and Q_3 were about 0.7. The additional R_2Q_3 term required to fit the data in this case appears to be associated with the presence of a more complex surface layer involving CuO, Cu₂O and CuCl phases.

The values of the parameters R (equivalent to the charge-transfer resistance) and the diffusion term, Q_2 , are shown as a function of time, for copper in the acidic solution, in the presence and absence of BTA, in Figure 3. Here it is seen clearly that the magnitude of

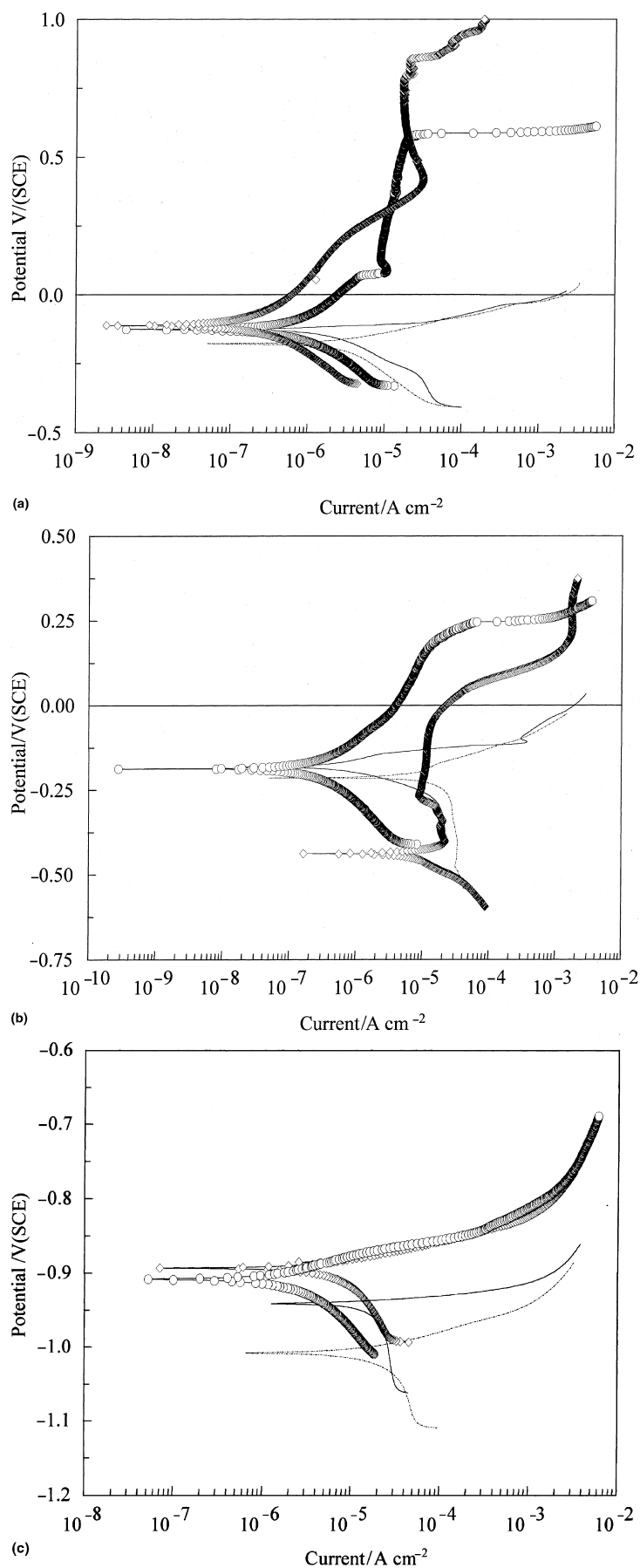


Fig. 1. Anodic polarisation plots recorded for Cu (a), CuZn (b) and Zn (c) in - - - 0.1 M NaCl, pH 3.5; — in 0.1 M NaCl, pH 7.8; ○ in 0.1 M NaCl, 0.01 M BTA, pH 7.8 and ◇ in 0.1 M NaCl, 0.01 M BTA, pH 3.5 solution.

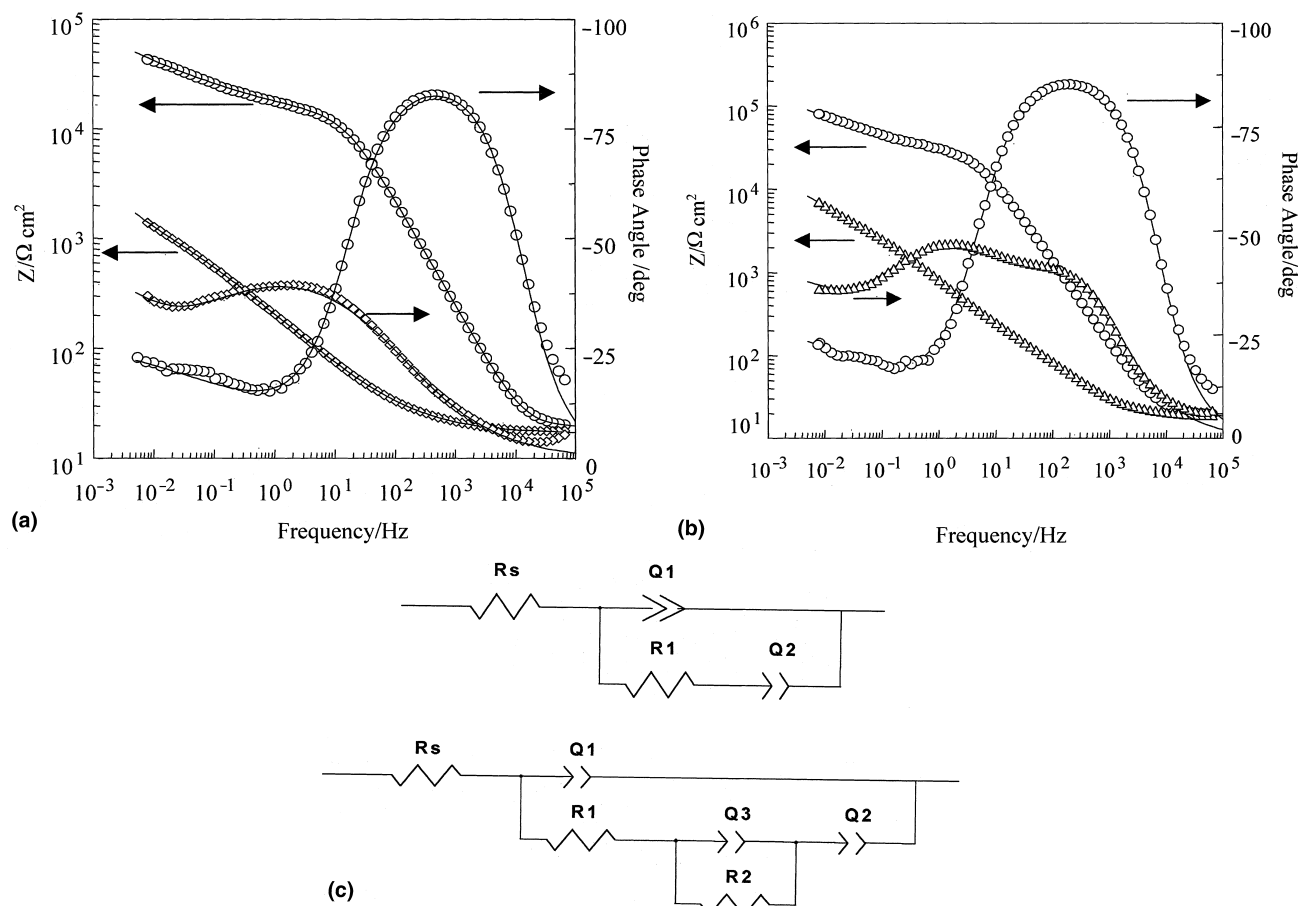


Fig. 2. (a) Impedance data recorded for Cu \diamond in 0.1 M NaCl, pH 3.5, \circ in 0.1 M NaCl, 0.01 M BTA, pH 3.5 solution, — simulated data; (b) \diamond in 0.1 M NaCl, pH 7.8, \circ in 0.1 M NaCl, 0.01 M BTA, pH 7.8 solutions, — simulated data; (c) equivalent circuits.

R , is increased considerably, and that the magnitude of Q_2 , equivalent to the diffusion process, is decreased considerably in the presence of BTA. It is also evident, from the near-constant R and Q values, that the BTA-produced films remain stable for periods in excess of 16 h. The value of Q_1 in the presence of BTA was of the

order of $0.5 \mu\text{F cm}^{-2}$ in the acidic solution and approximately $1.0 \mu\text{F cm}^{-2}$ in the near-neutral solutions compared to values of 800 and $100 \mu\text{F cm}^{-2}$ in the acidic and neutral solutions respectively in the absence of BTA. This low interfacial capacitance in the presence of BTA has been reported previously [25] and has been attributed to the formation of a polymer layer of BTA at the electrode surface. In this case, Q_1 is the sum of the double layer and the thin BTA polymer layer capacitance, i.e.

$$\frac{1}{Q_1} = \frac{1}{C_{\text{BTA}}} + \frac{1}{C_{\text{dl}}} \quad (1)$$

However, a reduction in the double layer capacitance, C_{dl} , may also occur with the replacement of water molecules by adsorbed organic molecules in the double layer, leading to a similar effect.

The impedance spectra recorded for Cu-37Zn, following a 460-min immersion period in the presence and absence of BTA, in the acidic and near-neutral solutions are shown in Figure 4(a) and (b) respectively. The same equivalent circuit was used to fit all the spectra and this circuit is shown in Figure 4(c). The circuit involves two RQ couples. The couple, R_1 and Q_1 , which represents the impedance data at high frequencies, is equivalent to

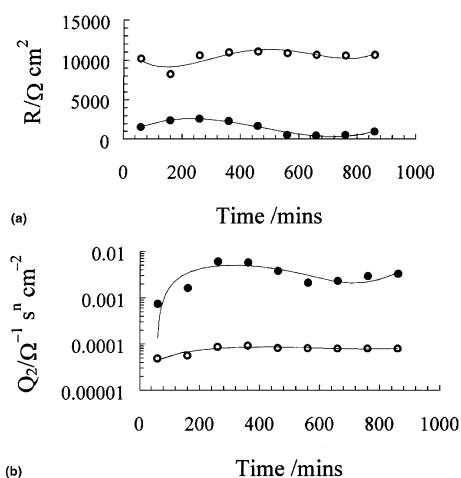


Fig. 3. (a) R plotted as a function of time for Cu \circ in 0.1 M NaCl, 0.01 M BTA, pH 3.5 and \bullet in 0.1 M NaCl, pH 3.5 solution; (b) Q_2 as a function of time \circ in 0.1 M NaCl, 0.01 M BTA, pH 3.5 and \bullet in 0.1 M NaCl, pH 3.5 solution.

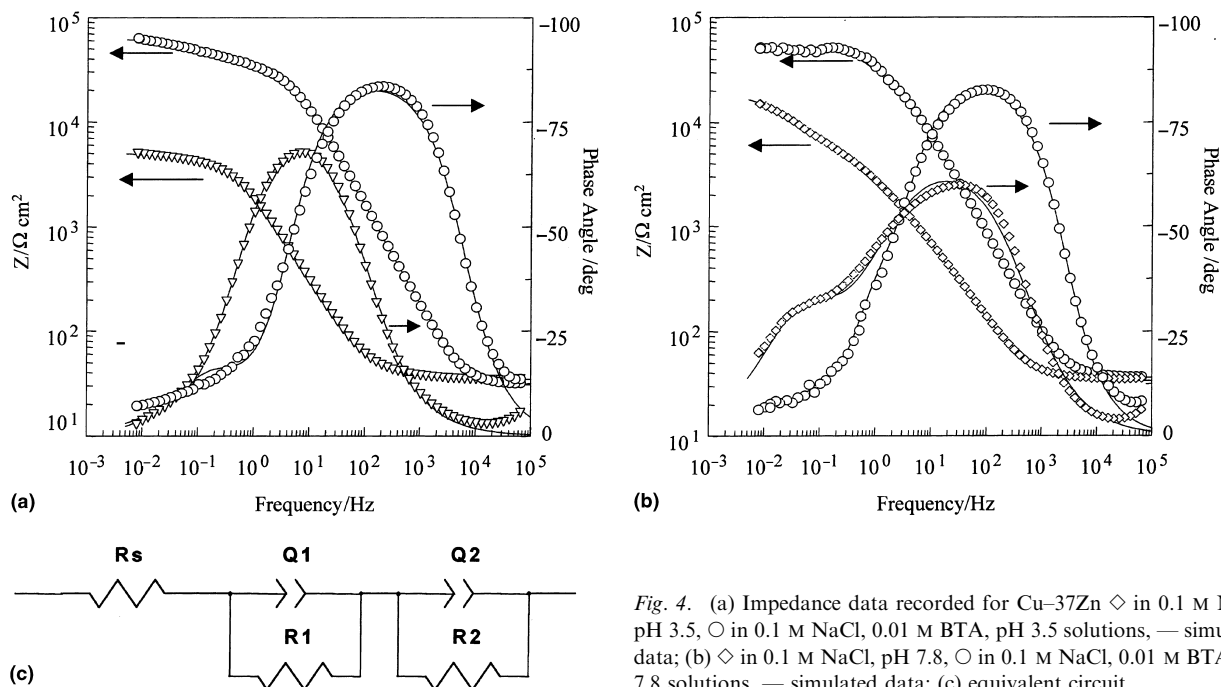


Fig. 4. (a) Impedance data recorded for Cu-37Zn \diamond in 0.1 M NaCl, pH 3.5, \circ in 0.1 M NaCl, 0.01 M BTA, pH 3.5 solutions, — simulated data; (b) \diamond in 0.1 M NaCl, pH 7.8, \circ in 0.1 M NaCl, 0.01 M BTA, pH 7.8 solutions, — simulated data; (c) equivalent circuit.

the faradaic charge-transfer process, with Q_1 being equivalent to the double layer capacitance C_{dl} . The couple, R_2 and Q_2 reflects the properties of the passive film, with Q_2 representing the capacitance of the film. This circuit was chosen as opposed to the circuits already shown for the Cu system as it provided fits with lower errors. It can be seen from the simulated data, shown as solid lines on the plots in (a) and (b), that good agreement between the simulated and actual experimental data is obtained. In the case of the acidic solution, a clear capacitive region was seen in the medium frequency region in the presence and absence of BTA. Here, Q_1 , the double layer capacitance, with n greater than 0.90, was of the order of $100 \mu\text{F cm}^{-2}$ in the absence of BTA, but was reduced to about $1.4 \mu\text{F cm}^{-2}$ in the presence of BTA. This is consistent with the data obtained for pure copper, where the low interfacial capacitance values can be attributed to the formation of a BTA-polymer layer at the electrode surface, or a modification of the double layer structure.

The n value for the Q_2 term was about 0.6 in the absence of BTA and approximately 0.8 in the presence of BTA, indicating that the passive layer is dominated by diffusion processes. Again, the magnitude of Q_2 was reduced on addition of BTA to the solution. The presence of BTA had an effect on the magnitude of both R_1 and R_2 . This can be seen clearly in Figure 5, where R_1 , R_2 , and $R_1 + R_2$ are plotted as a function of time for Cu-37Zn in the acidic chloride solution in the presence and absence of BTA.

The impedance data recorded for Cu-37Zn in the near neutral solution, Figure 4(b), are consistent with Q_1 and Q_2 being capacitor elements for the data recorded in the presence of BTA. In the absence of BTA the n values are about 0.7 for Q_1 and about 0.65 for Q_2 , indicative of some element of diffusion in the case of Q_2 . Again the

magnitude of these parameters was reduced considerably in the presence of BTA. Q_1 was of the order of $3 \times 10^{-6} \text{ F cm}^{-2}$ in the presence of BTA and $70 \times 10^{-6} \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ in the absence of BTA, while Q_2 varied from average values of $10 \times 10^{-6} \text{ F cm}^{-2}$ in the presence of BTA to $400 \times 10^{-6} \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ in the

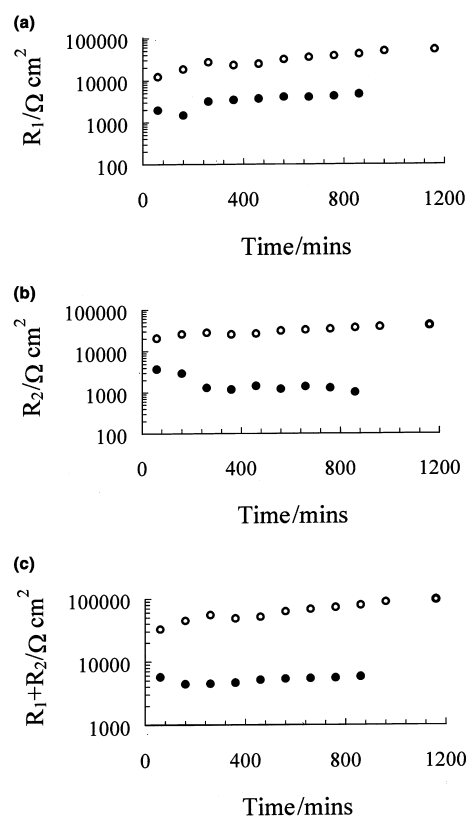


Fig. 5. R values plotted as a function of time for Cu-37Zn \circ in 0.1 M NaCl, 0.01 M BTA, pH 3.5 and \bullet in 0.1 M NaCl, pH 3.5 solution; (a) R_1 ; (b) R_2 ; (c) $R_1 + R_2$.

absence of BTA. As in the acidic chloride solution, the magnitudes of R_1 and R_2 were increased in the presence of BTA.

In Figure 6(a) impedance data recorded for pure Zn in the pH 7.8 chloride solution, in the presence and absence of BTA are shown. These data were recorded following a 460-min immersion period in the solution. Again, the solid lines represent the simulated data generated using appropriate equivalent circuits. The circuit used in fitting the data in the presence and absence of BTA is shown in Figure 6(b). In the simple circuit depicted in Figure 6(b), Q_1 corresponds to the double layer capacitance and R_1 to the charge transfer resistance. In the more complex circuit, Figure 6(b), the additional Q_3 , R_2 couple, which corresponds to the second time constant at low frequencies, appears to be connected with the presence of a corrosion film, while Q_2 corresponds to a Warburg impedance. The data obtained in the presence of BTA are characteristic of a one-time constant system, with a double layer capacitance of $1.8 \mu\text{F cm}^{-2}$. All the Q terms in the absence of BTA were intermediate between diffusion processes and capacitive processes, with n values ranging from 0.6 to 0.8. These Q terms were of the order of $560 \times 10^{-6} \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ for Q_1 , $550 \times 10^{-6} \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ for Q_2 and $2300 \times 10^{-6} \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ for Q_3 . Again, it is seen that the BTA-modified electrode exhibits a low interfacial capacitance.

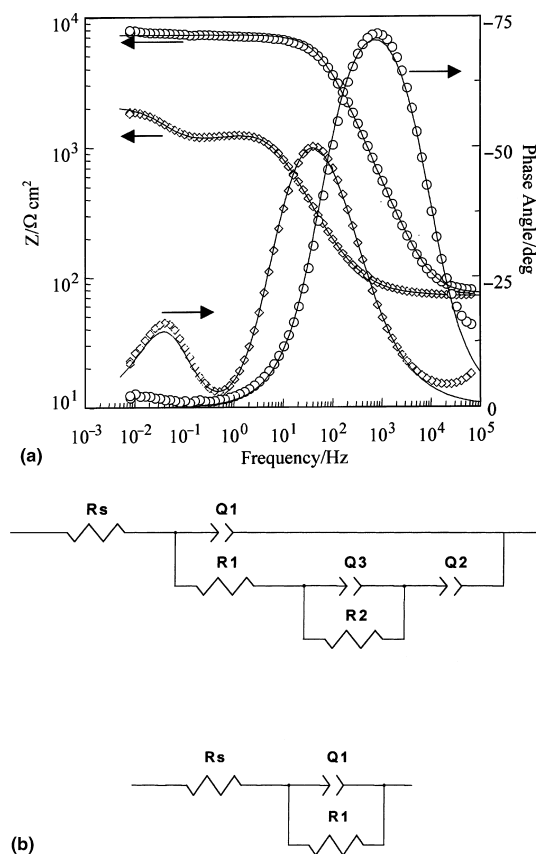


Fig. 6. (a) Impedance data recorded for Zn \diamond in 0.1 M NaCl, pH 7.8, \circ in 0.1 M NaCl, 0.01 M BTA, pH 7.8 solutions, — simulated data; (b) equivalent circuits.

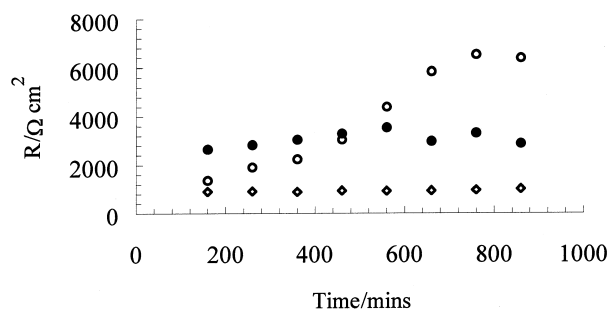


Fig. 7. R plotted as a function of time for Zn in \bullet 0.1 M NaCl, pH 7.8 solution; \circ 0.1 M NaCl, 0.01 M BTA, pH 7.8 solution; \diamond R_1 only.

As in the other systems the presence of BTA had a significant effect on the value of the charge transfer resistance, R . In Figure 7, R is plotted as a function of time for Zn immersed in the near-neutral solution in the presence and absence of BTA. In the case of the chloride solution R refers to the sum of R_1 and R_2 , while on a second plot R refers to R_1 only. During the early stages of immersion, up to 400 min, the charge-transfer resistance of Zn in the BTA-containing solution is comparable to R_1 and slightly less than R_{Tot} for the chloride-containing solution. But, on continued immersion, a significant increase in the charge-transfer resistance is seen in the BTA-containing solution. This may be connected with a somewhat slower rate of growth of the BTA polymer film, compared to the Cu-containing systems.

In Figures 8 and 9 voltammograms recorded for Cu and Cu-37Zn, following exposure to the acidic solution for 3 h and the near-neutral solution for 23 h, are shown. These measurements were carried out by immersing the electrode in the required solution and then polarising the electrode from 0 V(SCE), at a rate of 50 mV s^{-1} in the cathodic direction, down to -1.5 V(SCE) . In the case of the copper system, the spectra exhibit two characteristic peaks. The peak observed at about -200 mV(SCE) can be attributed to the formation of CuCl . The broad peak observed at the much lower potential of -1.25 V(SCE) may be associated with the presence of copper hydroxy species, probably the soluble species HCuO_2^- , Cu(OH)_2 , Cu(OH)_3^- or a mixture of these species, which form in alkaline and slightly alkaline solutions [26]. It may also contain a contribution from the reduction of Cu_2O , which appears at potentials close to this region [26]. However, this peak is reduced considerably in the presence of BTA in the near alkaline solution, but in the acidic solution the presence of BTA and the nucleation of a BTA-polymer film gives rise to conditions conducive to the formation of such copper-hydroxy species. But, the most interesting feature of these measurements is the fact that the CuCl peak is completely absent in the presence of BTA.

The voltammograms recorded for the Cu-37Zn system in the absence of BTA are consistent with a much more complex surface composition. Again, the presence of the CuCl peak is seen at about -200 mV(SCE) , but additional peaks at -0.5 V(SCE) ,

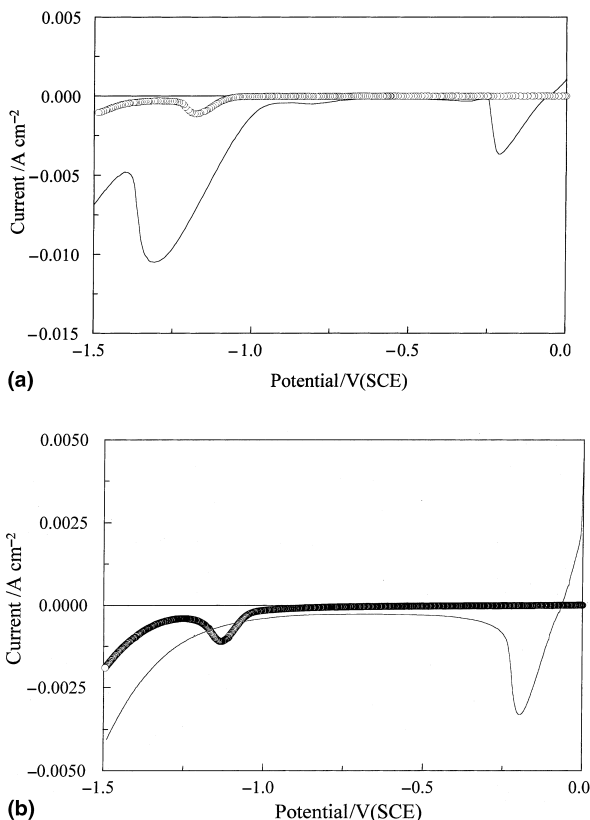


Fig. 8. Voltammograms recorded for Cu (a) following a 23 h immersion period in ○ 0.1 M NaCl, 0.01 M BTA, pH 7.8 — in 0.1 M NaCl, pH 7.8; (b) following a 3 h immersion period in ○ 0.1 M NaCl, 0.01 M BTA, pH 3.5 — in 0.1 M NaCl, pH 3.5.

−0.75 V(SCE), −1.0 V(SCE), −1.20 V(SCE), −1.25 V(SCE) and −1.3 V(SCE) are observed. The peaks at −0.5 V and −0.75 V may be attributed to the formation of CuO and Cu₂O respectively, while the peaks observed at potentials lower than −1.0 V(SCE) seem to be associated with copper hydroxy species and various zinc-containing corrosion products. However, in the presence of BTA, these peaks are removed and the only observed peak is that of the copper hydroxy species.

4. Discussion

It can be seen from the results presented that the presence of BTA in chloride solutions of pH 3.5 and 7.8 results in the passivation of pure Cu, Cu–Zn and to a lesser extent pure Zn.

The results presented, in the case of pure copper, agree well with the many published works on the effects of BTA on the corrosion susceptibility of copper [1–12]. Using the thermodynamic approach adopted by Tromans and co-workers [11], it can be deduced that in the pH 3.5 solution that CuCl₂[−] and CuCl are the stable phases under acidic conditions. Tromans and co-workers using the equilibria,

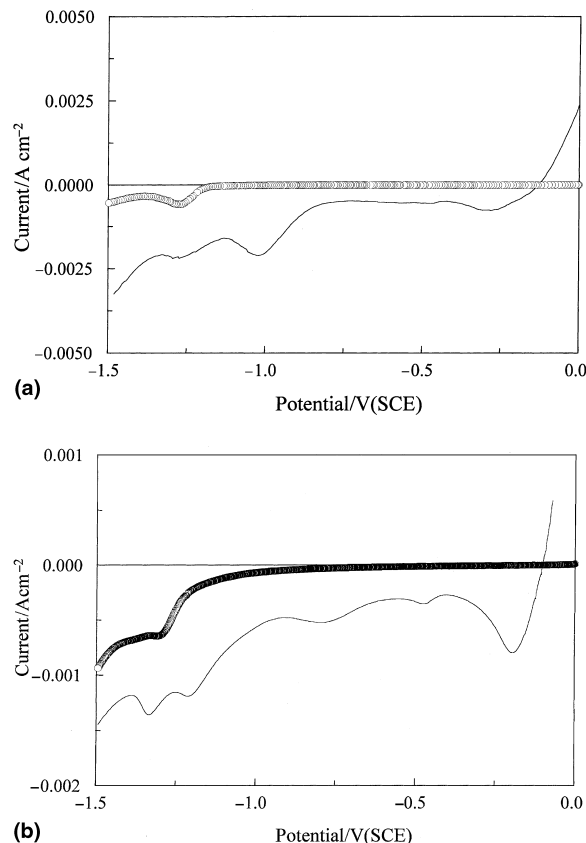


Fig. 9. Voltammograms recorded for CuZn (a) following a 23 h immersion period in ○ 0.1 M NaCl, 0.01 M BTA, pH 7.8 — in 0.1 M NaCl, pH 7.8; (b) following a 3 h immersion period in ○ 0.1 M NaCl, 0.01 M BTA, pH 3.5 — in 0.1 M NaCl, pH 3.5.



and the thermodynamic data,

$$E_{\text{CuCl}_2^-} = 0.224 - 0.0991 \log \left(\frac{[\text{Cl}^-]^2}{[\text{CuCl}_2^-]} \right) \quad (5)$$

$$E_{\text{CuCl/Cu}} = 0.117 - 0.0591 \log[\text{Cl}^-] \quad (6)$$

$$\log [\text{CuCl}_2^-] = \log [\text{Cl}^-] - 1.815 \quad (7)$$

have calculated the domains of stability of CuCl, CuCl₂[−], CuO and Cu₂O as a function of pH and Cl[−] activity. At the 0.1 mol dm^{−3} NaCl concentration used in this study, which is equivalent to an activity of 0.078, it can be seen from the data that CuCl is predicted to be the stable phase at pH values less than 5.0 and at applied potentials greater than 0.18 V(SHE). It is seen also that CuCl₂[−] species extend into the neutral and slightly alkaline pH regions and down to potentials as low as −0.1 V(SHE). Clear evidence for the formation of such chloride-containing species in the case of pure copper and the CuZn alloy is seen in the cyclic voltammetry measurements shown in Figures 8 and 9. The peaks observed at approximately −200 mV(SCE) can be attributed to the presence of CuCl and CuCl₂[−] species. The

potential at which these peaks appear, and the fact that more pronounced peaks are observed in the acidic chloride solution, is in good agreement with the thermodynamic data. Although the peaks are not as pronounced in the case of the CuZn alloy, Figure 9, there is clear evidence for the formation of these species on the CuZn electrode. However, in the presence of BTA these thermodynamically stable chloride-containing species are not formed.

In addition to the formation of CuCl corrosion products, CuZn electrodes are prone to dezincification [27, 28]. Indeed evidence in support of this dezincification in the chloride-containing solutions can be seen from the voltammograms shown in Figure 9, where the peaks may be assigned to different zinc and copper-containing corrosion products. However, it is clear that the voltammograms recorded in the presence of BTA are free from such zinc and copper corrosion products.

Evidence for the formation of a BTA-containing polymer film at the electrode interface can be seen from the interfacial capacitance values calculated in the presence of BTA. These values, regardless of the nature of the electrode, were of the order of $1 \mu\text{F cm}^{-2}$ in the presence of BTA. It is also interesting to note that the impedance data measured in the presence of BTA could, in all cases, be fitted to relatively simple equivalent circuits, whereas additional RQ couples to account for oxide/corrosion product phases were required to fit the data obtained in the BTA-free chloride-containing solutions. These data show clearly that the nucleation of a polymeric BTA film inhibits corrosion of the substrate material, and that these BTA polymeric films nucleate at Cu, Cu–Zn and at a somewhat slower rate on Zn surfaces.

The BTA films formed on pure copper are well known to involve the multi-layer structure of Cu/Cu₂O/Cu–BTA [29], a similar Cu–BTA layer is likely to form on the Cu–Zn alloy. Evidence for the formation of a polymeric layer on pure zinc is also obtained from the impedance data, particularly the interfacial capacitance. This layer inhibits the formation of zinc corrosion products, this can be seen from the impedance data presented in Figure 6, where the data recorded in the presence of BTA could be fitted to a simple Randles circuit, but the data recorded in the absence of BTA were typical of a more complex system, consistent with the formation of corrosion products. However, the BTA film produced on pure zinc appears to nucleate at a slower rate, evident from the time dependence of the polarisation resistance, Figure 7, than that observed with the copper systems.

5. Conclusion

A significant BTA-induced passivation effect was observed on polarising pure copper, pure zinc and a copper-zinc alloy electrode in acidic and near-neutral BTA-containing chloride solutions. This was evidenced from higher breakdown potentials and much higher

polarisation resistances, which were recorded for copper, zinc and copper-zinc in acidic and near neutral BTA-containing chloride solutions. A low interfacial capacitance was recorded for all three systems in the presence of BTA. This was attributed to the nucleation of a polymeric BTA-containing film at the electrode surface. The formation of copper and zinc-containing corrosion products were inhibited on nucleation of this polymeric film.

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